CHROMIUM STEEL ALLOYS AND ARTICLES MADE THREOF

Inventors: Oskar Pacher
Werner Lenoir

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[0002] Depending on their composition, steels have different levels of hydrogen solubility, the hydrogen being adsorbed by the steel surface and from there diffusing in atomic form into the iron lattice, where it is dissolved as an interstitial, accumulating in particular in the region of lattice defects. This explains the relatively high hydrogen solubility of cold-worked and/or hardened steels. The dissolved hydrogen, in particular in ferritic steels with an increasing yield strength, reduces the ductility, in particular the elongation at break. This can be explained by the fact that the hydrogen, in the region of cracks, is intercalated in front of the crack tip in the elongated iron lattice, and, as the hydrogen concentration increases, leads to further cracking or crack propagation as a result of cleavage fracture. This crack propagation is by its nature dependent on the concentration of the dissolved hydrogen

and accordingly on the hydrogen solubility of the corresponding steel.

[0003] The hydrogen uptake in the steel is not only dependent on the composition of the steel: it is also influenced to a considerable degree by physical parameters. For example, in the case of welding with coated electrodes and in the case of submerged-arc welding, the moisture which is present in the electrode shell or in the powder leads to a considerable hydrogen uptake in the weld material and in the base material. Furthermore, there is a particularly high risk of hydrogen uptake in the case of hardened steels and in the event of electrolytic coating. During the coating, hydrogen is also simultaneously deposited cathodically together with the metal. This hydrogen has an embrittling effect both in the coating and in the base material.

[0004] In the case of bandsaw blades, which are usually guided over two rolls and therefore per revolution undergo a double diversion of 360°, the tendency toward hydrogen embrittlement may play an important role. Endless bandsaw blades or bimetal saw bands generally comprise a support band, the ends of which are butt-welded to one another and which is fitted with cutting teeth made from high-speed steel or cemented carbide. However, the wear resistance of cutting teeth of this type is insufficient for very hard and brittle materials, such as silicon, intermetallic compounds, ceramic and rock. Therefore, German laid-open specification 37 02 795 A1 proposes the use of endless bandsaw blades, the cutting edge of which is provided

with vapor-deposited diamond particles. Although an endless band of this type allows clean cuts to be made and also has a considerably longer service life than bimetal saw bands, difficulties arise during the vapor deposition of the diamond particles, on account of the high temperatures which are required, of the order of magnitude of 800 to 1000°C, with a duration of action of 5 to 16 hours. However, this has an adverse effect on the support band, shortening its service life.

[0005] Circular saw blades, the periphery or cutting teeth of which have an electrolytically applied metallic coating with intercalated diamond particles, are also known. However, the electrolytic coating inevitably also leads to the deposition of hydrogen from the electrolyte and therefore to harmful embrittlement of the saw blade periphery. However, this is less problematical in the case of circular saw blades than in the case of bandsaw blades, since circular saw blades are not subject to any significant reverse bending loads. An inevitable disadvantage of circular saw blades, however, results from the fact that their cutting edge is not tensioned, and therefore the cutting result is adversely affected by vibrations and distortion. An internally cutting circular saw blade in the form of an annular disk with a diamond-coated cutting edge made from a steel alloy comprising at most 0.10% of carbon, over 1.0% to at most 3.0% of silicon, less than 0.5% of manganese, 4.0 to 8.0% of nickel, 12 to 18% of chromium, 0.5 to 3.5% of copper, at most 0.15% of nitrogen and at most 0.004% of sulfur, and a total carbon and nitrogen content of at least 0.10%, as is known from

US patent 4,847,168, seeks to avoid this drawback. The circular saw blade is suitable for cutting semiconductor materials; on account of its high silicon content after the cold-working, it has a substantially martensitic microstructure, which in the case of electrolytic coating is particularly subject to hydrogen embrittlement.

[0006] Although a circular saw blade of this type avoids the harmful vibrations as a result of the vibrations which are formed at the internal cutting edge being damped to a sufficient extent as a result of the surface area of the saw blade increasing toward the outside, this advantage is only achieved by virtue of the fact that only the short diamond-tipped edge of the central saw blade opening is available for cutting purposes. The short cutting edge length inevitably leads to more rapid wear and/or a shorter service life and therefore requires the saw blade to be changed frequently. A further drawback of internally cutting circular saw blades is that the dimensions of the material being cut are dependent on the limited diameter of the cutting opening in the circular saw blade.

[0007] By contrast, bandsaw blades have a very long cutting edge and moreover can also be operated with different levels of stress; however, on account of the double 360° diversion per revolution and the high rotational speed, they require a high level of reverse bending strength. Although there is a range of alloyed steels with a high reverse bending strength, these steels are not suitable for electrolytic application of a metal layer with embedded diamond particles, since their reverse

bending strength is lost as a result of hydrogen embrittlement caused by the uptake of hydrogen during the electrolytic deposition.

[0008] A further drawback of diamond-coated saw blades is that at elevated temperatures diamond is converted into graphite, which can lead to complete loss of the hardness and the bonding in the metallic embedding material. Therefore, the hardening of the support band has to take place prior to the coating operation. However, this entails a new problem, since with hardened steels there is a particularly high risk of hydrogen uptake during pickling and during an electrolytic coating operation from the corresponding acid or a thermal coating operation from the vapor phase as a result of hydrogen being released from hydrocarbons.

[0009] The invention is based on the problem of providing a steel alloy having a high hydrogen stability even in the hardened state which is suitable in particular as a material for bandsaw blades which are coated with hard-material particles and have a high reverse bending strength and wear resistance.

[00010] To achieve this, the invention proposes the use of a chromium steel alloy comprising 0.25 to 0.35% of carbon, 0.3 to 0.5% of silicon, 0.8 to 1.5% of manganese, 1.0 to 2.0% of molybdenum, 1.5 to 3.5% of chromium, 0.5 to 1.5% of nickel, 0.5 to 2.5% of tungsten, 0.15 to 0.30% of vanadium and/or 0.05 to 0.10% of niobium, 0.05 to 1.0% of copper, 0.01 to 0.2% of aluminum and 0.01 to 1.0% of cobalt, remainder iron including smelting-related impurities.

[00011] A steel alloy comprising 1.2 to 1.8% of molybdenum, at most 2.5% of chromium, 1.2 to 1.8% of tungsten and 0.1 to 0.8% of copper, individually or in combination, is particularly suitable.

[00012] The hydrogen stability is particularly high if the ratio of the tungsten and molybdenum contents is of the order of magnitude of 1 and/or if the steel contains niobium and vanadium simultaneously.

[00013] The steel alloy according to the invention has a hardness of 450 to 550 HV, corresponding to a tensile strength of 1650 to 1850 N/mm^2, and on account of its high resistance to (hydrogen) embrittlement is particularly suitable as a support material for objects coated electrolytically, by PVD or by CVD (PVD = physical vapor deposition; CVD = chemical vapor deposition), such as bandsaw blades. Suitable hard-material particles include diamond, cubic boron nitride, sintered carbide and corundum.

[00014] The high hydrogen stability of the steel alloy according to the invention allows the cold-worked support band to be heat-treated prior to the coating operation in the production of bandsaw blades without the presence of hydrogen leading to (hydrogen) embrittlement during the coating operation. At the same time, as a result of the heat treatment having been "brought forward", the risk of diamond being converted into graphite during the hardening which is otherwise required following the coating operation, as is required for

steel alloys which are not sufficiently hydrogen-resistant, is also eliminated as a result.

[00015] On account of its hydrogen stability, the steel alloy according to the invention is particularly suitable for electrolytic coating, which usually takes place at low temperatures of up to 80°C. However, prior to the coating operation it is necessary to carry out a pickling operation using acids to remove surface oxides so as to create a sufficient bonding base for the coating. Hydrogen is always also formed during the pickling and coating by electrodeposition, and in the case of materials which are not sufficiently hydrogen-resistant, this hydrogen diffuses into the metal lattice, having an adverse effect on the reverse bending strength. This risk is particularly high in the case of pickling, since it produces large amounts of hydrogen which enters the metal lattice in atomic form.

[00016] The heat treatment of the steel alloy according to the invention preferably comprises an austenitization treatment at 1150 to 1200°C, preferably at most 1190°C, followed by quenching to room temperature and tempering at 450 to 600°C, preferably at at least 480°C. To set a hardness of, for example, from 450 to 550 HV, the steel alloy can be tempered two or three times at the abovementioned temperatures.

[00017] The support band only needs to be coated in the region of its cutting edge and/or the cutting teeth, for example over 10 to 60% of its surface area, and then only requires an insulating covering in the region outside the intended coating.

Prior to the coating operation, it may be necessary for the bandsaw blade to be cleaned by pickling with an acid.

[00018] The high hydrogen stability of the steel alloy according to the invention ensures that there is no unacceptable uptake of hydrogen from the pickling solution.

[00019] The coating preferably consists of hard materials or of a material which serves as an embedding material for the hard-material particles and may contain titanium, aluminum, nickel, copper, tin, carbon, nitrogen and oxygen, for example carbides, such as titanium carbides, or carbonitrides, titanium aluminum nitrides and oxides such as Al_2O_3. A soft coating is also possible, if it is subsequently hardened.

[00020] The invention is explained in more detail below with reference to exemplary embodiments and the drawings, in which:

[00021] Fig. 1 shows a block diagram presenting the individual process steps involved in the production of a saw band,

[00022] Fig. 2 diagrammatically depicts a test apparatus for determining the reverse bending strength,

[00023] Fig. 3 shows a graph illustrating the hydrogen uptake as a function of the limit bending value N_O, and

[00024] Fig. 4 shows a graph illustrating the hydrogen uptake K as a function of the limit bending value N_B.

[00025] Table 1 below gives the compositions of three steel alloys E1 to E3 according to the invention, on the one hand, and of four conventional comparison alloys V1 to V4, as are used to produce conventional bimetal saw bands as support band material.

[00026] *Table I*

Alloy	C (%)	Si (%)	Mn (%)	Mo (%)	Cr (%)	Ni (%)	W (%)	V (%)	Nb (%)	Cu (%)
E1	0.28	0.40	0.90	1.35	2.0	0.90	1.30	0.22	0.05	0.08
E2	0.30	0.38	1.08	1.50	2.0	0.95	1.50	0.28	0.10	0.15
E3	0.33	0.33	1.00	1.08	1.9	0.80	1.05	0.15	0.08	0.22
V1	0.26	0.20	0.40	2.40	3.8	0.45	0.05	0.21	0.01	0.05
V2	0.34	0.35	0.95	1.95	3.1	0.70	0.10	0.05	0.01	0.05
V3	0.46	0.25	0.61	0.95	1.2	0.50	0.01	0.30	0.005	-
V4	0.65	0.26	0.70	-	-	-	-	-	-	-

[00027] For the tests, cold-rolled strips with a thickness of 0.9 mm and a width of 15 mm were produced from the steels listed in Table I. Test specimens were produced therefrom. In each case two different heat treatments were carried out, in order to set different hardnesses. For this purpose, specimens E1 to V3 were austenitized at a temperature of 1180 or 1190°C, quenched in water and tempered three times at 540°C. Specimen V4, by contrast, was austenitized at 820°C and tempered twice at 300°C. A test apparatus whose basic principle is illustrated in Fig. 2 was used to determine the limit bending values N_O and N_B, i.e. the number of times that hydrogen-free specimens (N_O) and hydrogen-laden specimens (N_B) could be bent before fracture occurred.

[00028] The test apparatus had clamping jaws with a curved clamping surface which allowed the specimen to be bent back and forth. A driver was arranged on a sliding carriage in such a way that it was possible for the specimens to be laterally deflected through 30 mm. This sliding carriage was moved horizontally by

means of a connecting rod and an electric motor with step-down transmission. The bending tests were carried out until the specimen fractured. The fracture was detected electronically and the number of bending operations recorded as a numerical value (N_O and N_B).

[00029] To determine the Vickers hardness HV1, the specimens were subjected to a load of 10 N, the diagonals of the diamond pyramid (136° tip angle) were measured automatically and the hardness values were displayed digitally.

[00030] To assess the hydrogen sensitivity or the limit bending value N_B, the specimens were immersed at room temperature, individually, as cathode in a 15% strength sulfuric acid, and a DC voltage of 6 volts was applied for three minutes. The counterelectrode used was graphite with an approximately 20% larger surface area. During this treatment, cathodic hydrogen was formed on the surface of the specimen, rising upward in small bubbles but partially also penetrating into the metal.

[00031] The reverse bending strength of the specimens which had been laden with atomically dissolved hydrogen in this way was then tested with the aid of the test apparatus shown in Fig. 2. The number of bending operations N was a characteristic indicator of the hydrogen uptake or the hydrogen embrittlement K.

[00032] The data from the tests for in each case two specimens of the same composition but which have undergone different heat treatments and accordingly also have a different hardness are compiled in Table II below.

[00033] *Table II*

Test	Alloy	RM (N/mm^2)	HV	N_O	N_B	K
1	E1	1787	478	25 373	23 771	6.3
2	E1	1802	520	29 973	27 354	8.7
3	E2	1796	485	28 105	26 371	6.2
4	E2	1805	515	28 212	26 506	6.0
5	E3	1775	436	24 164	23 258	3.7
6	E3	1815	525	30 132	27 288	9.4
7	V1	1698	447	19 312	15 231	21.1
8	V1	1765	480	25 686	18 798	26.8
9	V2	1735	475	24 362	19 475	20.1
10	V2	1783	490	26 017	20 572	20.9
11	V3	1785	485	19 954	16 581	16.9
12	V3	1805	502	22 371	17 899	20.0
13	V4	1790	560	17 381	13 251	23.8
14	V4	1875	596	26 352	16 352	37.9

[00034] In the above table:

Rm: is the tensile strength in the hardened state in N/mm^2 (without hydrogen loading);

HV: is the Vickers hardness;

N_O: is the number of bending operations until fracture in the case of the specimens which are not laden with hydrogen; and

N_B: is the number of bending operations for the specimens which had been electrolytically laden with hydrogen.

[00035] Each of the alloys tested has its own N_O value for the limit bending value. If the alloy is laden with hydrogen, a different limit bending value N_B results, which is lower than N_O. The reduction in the limit bending value on account of the loading with hydrogen is given by the difference (N_O-N_B). If this is related to N_O and multiplied by 100, the result is a K value:

$$K = 100\frac{N_O - N_B}{N_O}$$

as a characteristic indicator of the hydrogen stability. Low K values are a reliable indication of a high hydrogen stability.

[00036] The results of the bending tests with the unladen specimens are illustrated in graph form in the diagram shown in Fig. 3, demonstrating that hydrogen uptake always occurs, since none of the measured values is in the region of K = 0. However, a comparison between the individual values reveals that the K values for the specimen dots according to the invention are grouped below a K value of 10 with maximum limit bending values N_O of approximately 24 000 to 32 000, while the comparison specimens (triangles) are substantially at a level above a K value of 20. Comparison alloy V4, which is an unalloyed conventional carbon-rich saw blade material, has the highest K value.

[00037] The superiority of the steel alloy according to the invention is expressed particularly clearly in the diagram shown in Fig. 4, which illustrates the K values as a function of N_B for the specimens which had been electrolytically laden with hydrogen. The slight differences between the limit bending

values of the steel alloys E1 to E4 according to the invention by comparison with the values shown in the diagram presented in Fig. 3 are attributable to hardness differences which have been deliberately set in these alloys and to natural scatter. The improvement to the hydrogen stability is demonstrated particularly clearly if the specimen E1 according to the invention is compared with the comparative specimen V8 with approximately the same hardness and strength.

[00038] For coating purposes for sawing tests, band strips with a length of 1600 mm and a width of 15 mm made from alloys E1, E2, V3 and V4 were covered on both sides, starting from the band spine, with a PVC adhesive tape over a width of 10 mm. Then, the uncovered cutting edge region was electrochemically pickled and electrolytically coated with nickel in an electroplating tank. During the coating, diamond particles were incorporated in the nickel layer by means of a directional flow. On account of the electrically insulating covering, the specimens were only coated in the uncovered cutting edge region. After the coating operation, the saw band was rinsed clean, dried, the adhesive tape was removed and the ends were joined to one another by butt-welding to form an endless band. In a second series of tests, the cutting edge region of a saw band, after initial base-coating with nickel in an electroplating tank, was transferred to a plasma spray chamber in order for a second layer comprising nickel and molybdenum as well as corundum powder and zirconium oxide granules to be applied to the existing electrolytic base-coating.

[00039] An aluminum-silicon cast alloy, which on account of its high silicon content was difficult to saw, was used for the sawing tests.

[00040] With the saw bands made from alloys E1 and E2 which had been electrolytically coated and covered with diamond grains, 320 and 365 cuts, respectively, with a flatness deviation of < 20 μm were possible with a saw stress of 240 N/mm^2.

[00041] With the comparison saws made from alloys V3 and V4 with the same stress, only 75 and 55 cuts, respectively, were possible. After these tests, the saw stress was reduced by 40%, whereupon the number of sawing cuts rose to 278 and 310, respectively. However, this led to a deterioration in the flatness deviation to on average 120 μm. This drop in the cutting quality is the direct consequence of the saw stress being too low, which has to be the case in particular with hydrogen-damaged steels on account of their embrittlement.